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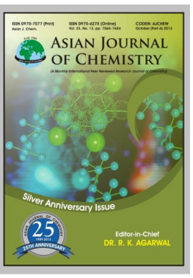

Synthesis and Application of 2,3-Dihydroxybutanedioic Acid Esters as Efficient Additives in Methanol-Gasoline

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In this paper, 2,3-dihydroxybutanedioic acid esters (tartaric esters) were synthesized and used as phase stabilizer and saturation vapour pressure depressor of methanol-gasoline. The results show that the stabilities of the methanol-gasoline depend on the length of the tartaric esters' alkoxy group. Several tartaric esters were found to be effective in various gasoline-methanol blends and the tartaric esters display high capacity to depress the saturation vapour pressure of methanol-gasoline. According to the results, it can be concluded that the tartaric esters have the great potential to be bifunctional gasoline-methanol additives.

Key Words: Methanol-gasoline, Tartaric esters, Phase stability, Evaporation.

INTRODUCTION

Facing on the rising huge consumption of oil, development of clean and alternative fuels increasingly draws worldwide attentions[1]. In a large number of alternative fuels, methanol displays fine combustion properties similar to gasoline and has advantages such as high octane number, low emissions, antiknock, rich resource, mature technology, *etc*., so it can be used as alternative fuel for gasoline[2]. In recent years, extensive research of the low percentage methanol-gasoline has been carried out and it has been applied in Shanxi, Sichuan, Zhejiang, Inner Mongolia, Shaanxi, Xinjiang and other places of China gradually [3]. However, there are several problems needing to resolve in methanol-gasoline research, in which the phase stability is the most important one. One of the popular solutions is to add phase stabilizer to reduce alcohol-oil interfacial tension[4,5], such as ethers, ketones, esters, fatty alcohols, aliphatic hydrocarbons, fatty acids, non-ionic surfactants, acetal/ketones, biodiesels and amidines[6-11]. Secondly, the low boil point of methanol leads to high possibility of vapour lock by raising the vapour pressure of methanol-gasoline[12-14]. The current solution for vapour lock is to add pressure reducers, such as aliphatic ketones, fatty acids, fatty aldehydes, fatty ethers, acetals/ketals, *etc*.[15-24]. At present, few researches have carried out to develop bifunctional additives with the abilities of both phase stability and vapour pressure depressing for methanol-gasoline. In this work, a series of 2,3-dihydroxybutanedioic acid esters (tartaric esters) was synthesized and screened in the methanol-gasoline as a bifunctional additive.

EXPERIMENTAL

All the solvents were AR grade and purchased from Xi'an Chemical Agent Co and the 93# gasoline is commercially available. The phase stabilizing and pressure reducing were tested on DFY-cryostat instrument (Xi'an Yuhui Instrument Co. Ltd.) and DSL-080 vapour pressure detector (Dalian the Ceon Electronic Equipment Co. Ltd.).

Synthesis of tartaric esters

Method A: Tartaric acid (23 g), methanol (18 mL) and *p*-toluenesulfonic acid (TsOH) (0.6g) was added to the flask. After 10 h of refluxing, the reaction mixture was cooled to room temperature. Methanol and methyl tartaric were distillated, respectively. The synthesis of ethyl tartaric and propyl tartaric is same to method above[25].

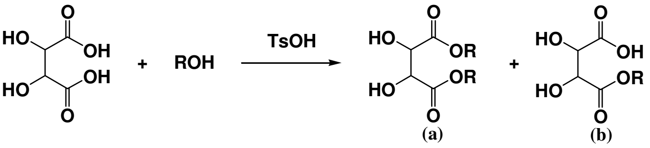
Method B: Tartaric acid (0.15 mol), *n*-butanol (0.45 mol), cyclohexane (30 mL), *p*-toluenesulfonic acid (0.5 g) were refluxed for 5 h and the produced water was separated by a water separator. After cooled to room temperature, cyclohexane, *n*-butanol and *n*-butyl tartaric were separated by vacuum distillation. The synthesis of amyl tartaric ester, hexyl tartaric ester, hepyl tartaric, octyl tartaric ester and decyl tartaric ester is same to method above[26,27].

Phase stability test: The fuel blends were prepared by blending 15, 30, 50 and 65 vol. % of methanol with base gasoline and the fuel blends were assigned as M15, M30, M50 and M65. The phase stabilizing tests were carried out according to Chinese National standards of GB 8017-87, GB/T 23799-2009, DB61/T 352-2004 and DB51/T 448-2004. First the test tube full of methanol-gasoline with different ratios was placed in a cryostat and then the temperature was adjusted from 40-25 ºC. At each degree, the tube was taken out and was shaken for two to three seconds and the phase separation temperature was determined as the solution becomes cloudy[28-30].

Vapour pressure test: The effect of tartaric esters on vapour pressure of methanol-gasoline was investigated according to Chinese standards of GB 8017-87. The methanol-gasoline was poured into the vapour pressure detector and put into the water bath of 37.8 ºC. The methanol-gasoline was intensive mixed by taking the detector from the water bath every 5 min and reversing violently. The operation was repeated until the pressure becomes steady.

RESULTS AND DISCUSSION

Synthesis of tartaric esters: The reaction of tartaric acid and alcohols are shown in **Scheme-I** and both the reaction conditions and the yield are summarized in Table-1. In this reaction, diester (a) is the main product and the monoester (b) is the undesired byproduct. To reduce the byproduct, high quantities of alcohol was used. For the synthesis of the first three esters, the alcohols were employed with higher ratio over 1:30. For the rest esters, the tartaric acid and alcohol ratio is as high as 1:5. The yields were obtained in the range from 60.2 to 77.6 % as shown in Table-1.



Scheme-I: Reaction of tartaric acid and alcohol

TABLE-1
RESULTS OF THE SYNTHESIS OF TARTARIC ESTERS

Esters	Tartaric acid:alcohol	Method	Yield (%)
Methyl tartaric	1:30	A	70.9
Ethyl tartaric	1:30	A	71.1
Propyl tartaric	1:30	A	76.5
Butyl tartaric	1:5	B	77.6
Amyl tartaric	1:5	B	64.5
Hexyl tartaric	1:5	B	60.2
Hepyl tartaric	1:5	B	72.1
Octyl tartaric	1:5	B	71.5
Decyl tartaric	1:5	B	72.2

Effect of tartaric ester on the phase stability of methanol-gasoline: The phase stabilities of tartaric esters for the methanol-gasoline blends of M15, M30, M50 and M65 at different temperatures from -25 ºC to 40 ºC were investigated and summarized in Figs. 1-4. The experimental data indicate that the length of carbon chain of tartaric ester effects on the phase stability of methanol-gasoline significantly. For the esters with very short, such as methyl tartaric, ethyl tartaric, the phase stability to methanol-gasoline are ineffective, even as the dosage over 10 %, methanol and gasoline homogenized blends can not obtained in M15, M30, M50 and M65 at 40 ºC. The reason may be due to the strong hydrophilic property but weak lipophilic property of short-carbon-chained tartaric ester, leading them not to dissolve in gasoline. With the increase of the carbon chain of tartaric esters, lipophilic property of the ester is markedly enhanced and the dissolution in gasoline is intensified, resulting in higher solubilization in the various blends. According to the results, it can be found that long-carbon-chained tartaric esters are with the effective phase stability to methanol-gasoline. The phase separation temperatures of the four methanol-

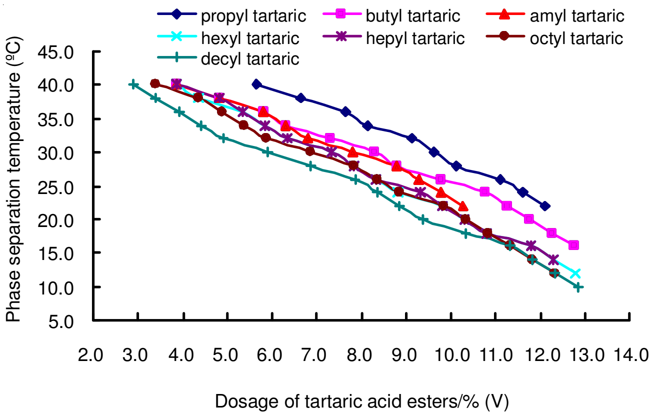


Fig. 1. Effect of the tartaric ester dosage on the phase stability of M15. (The dosages of methyl tartaric and ethyl tartaric are beyond 11.1 % at 40 ºC)

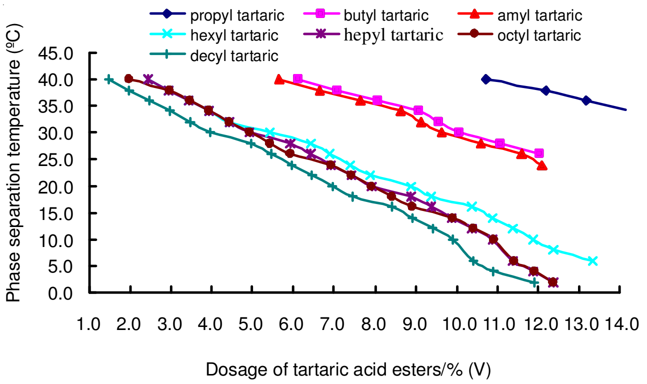


Fig. 2. Effect of the tartaric ester dosage on the phase stability of M30. (The dosages of methyl tartaric and ethyl tartaric are beyond 11.1 % at 40 ºC)

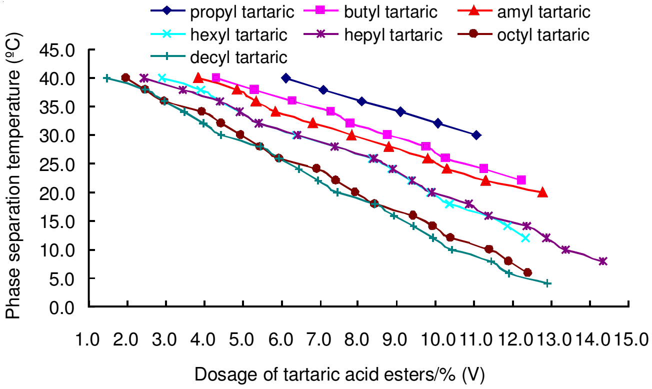


Fig. 3. Effect of the tartaric ester dosage on the phase stability of M50. (The dosages of methyl tartaric and ethyl tartaric are beyond 11.1 % at 40 ºC)

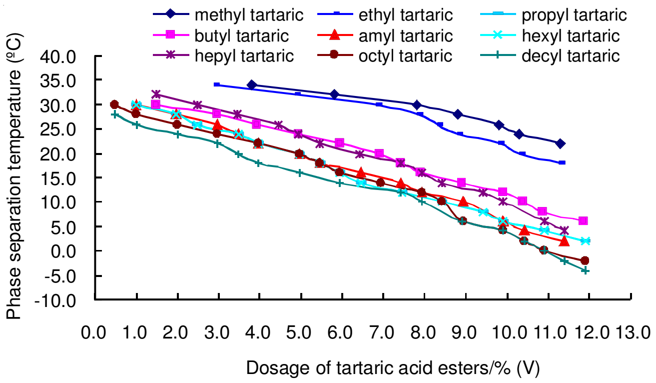


Fig. 4. Effect of the tartaric ester dosage on the phase stability of M65

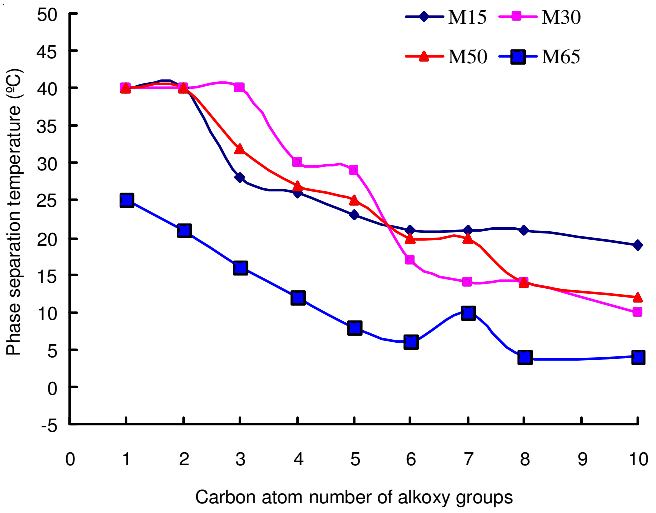


Fig. 5. Relationship of the alkoxy groups and the phase separation temperature

gasoline blends with the ester dosage of 10 % was estimated and shown in Fig. 5. It can be found that the phase separation temperature declines along with the length of the alkoxy group. For M15, the phase separation temperature comes to the lowest as the carbon atom number of alkoxy group comes to 6. For M30, the carbon atom number of alkoxy group comes to 7. For M50, the carbon atom number of alkoxy group comes to 8. For M65, the lowest phase separation temperature was obtained as the carbon atom number of alkoxy group comes to 8.

Effect of tartaric ester on the evaporation of methanol-gasoline: The saturation vapour pressure will rise over that of gasoline as it blends with low percentage methanol such as M15 and M30, which will lead to vapour block as it used under relative high temperature. Some chemicals with lower saturation vapour pressure can be added to depress the high pressure of gasoline. In this work, the effect of tartaric ester on the saturation vapour pressure of M15 methanol-gasoline was investigated referred to GB 8017-87 "petroleum products the vapour pressure determination method (Reid Method)" and the results are shown in Fig. 6. The original saturation vapour pressure of M15 is 63.5 kPa, which is 5.7 kPa higher than that of gasoline. As little amount of esters were added in, the saturation vapour pressure was depressed obviously. With the esters' dosage of 0.1 %, methyl tartaric ester, ethyl tartaric ester, propyl tartaric ester, butyl tartaric ester, amyl tartaric ester, hexyl tartaric ester and decyl tartaric ester can depress the saturation vapour pressure lower than that of gasoline, among which decyl tartaric ester is the most effective one. Further increase of the dosage depresses the saturation vapour pressure ineffectively. The main reason is contribute to the distribution of tartaric esters on the surface of methanol-gasoline, which prevent the formation of an azeotrope with low boiling point.

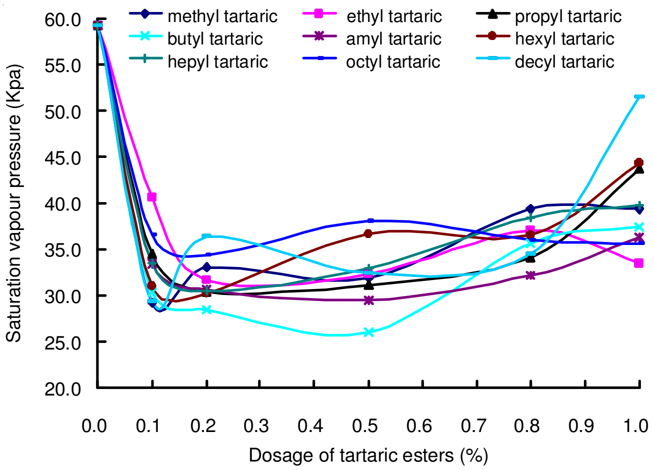


Fig. 6. Effect of tartaric esters on the evaporation of methanol-gasoline M15 system

Conclusion

Tartaric esters were synthesized and screened for their performances of phase stabilizing in M15, M30, M50 and M65 and pressure reducing in M15. The results show that the length of alkoxy group of tartaric esters effects on the phase stability of methanol-gasoline significantly. The phase stability of tartaric esters with long length is more potent than that with short length. All of the synthesized esters are potent to depress the saturation vapour pressure of methanol-gasoline. With the dosage of 0.1 %, all tartaric esters can depress the saturation vapour pressure lower than that of gasoline and decyl tartaric ester is the most effective one.

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